Ammonia Cracking for Hydrogen Production Using Microwave Plasma Jet of Argon

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Abstract: A rapid conversion from ammonia to hydrogen is a critical part of the ammonia-hydrogen economy due to the toxicity and low reactivity of ammonia that limit its terminal application. To this end, this work explored the performance of a microwave surface discharge plasma (surfatron) jet in cracking Ammonia (NH_3) without using any catalyst at atmospheric pressure. A range of total flow, NH_3 content, and input microwave power were adopted to test the influence of experimental conditions on the NH_3 conversion. Both optical emission spectroscopy (OES) and Fourier Transform Infrared Reflectance Spectroscopy (FTIR) were utilized to gain knowledge about the mechanism of ammonia conversion. Results showed that the NH_3 conversion ratio reached almost 100% at a total flow of 1 SLPM (standard liter per minute) with an ammonia content of 0.5% when microwave power is 100 W. Decreasing the input microwave power or increasing the total flow rate reduced the NH_3 conversion ratio. The energy density (defined as the input power divided by the total flow rate) was found to be a critical factor characterizing the NH_3 conversion. Moreover, the temperature measurement with OES showed that the rotational temperatures were very close to each other under different powers and total flows, implying that the residence time in the plasma region was the most important factor in NH_3 conversion in the present experiment.

Keywords: Ammonia conversion, hydrogen production, microwave plasma, atmospheric pressure, energy density

1. Introduction

Ammonia and hydrogen are considered as one of promising alternative fuels for the coming carbon-neutral society. However, the toxicity and low reactivity of ammonia limit its terminal application, while the explosion hazard of hydrogen also brings about problems in transportation. A feasible strategy is considering ammonia as a hydrogen carrier and using it for transportation, and for the terminal application, ammonia could be cracked to obtain hydrogen. Therefore, a rapid transformation from ammonia to hydrogen is of great importance for this ammonia-hydrogen economy.

Atmospheric pressure plasma is a promising source to crack ammonia. According to the temperature difference between the electron and bulk gas, plasma can be divided into equilibrium plasma and non-equilibrium plasma. In equilibrium plasma, e.g., arc plasma, the electrons are in thermal equilibrium with the gas molecules, and both are usually in a temperature above 10^4 K. However, due to this extremely high temperature, thermal erosion is very likely to occur and cause irreversible damage to the electrodes. On the other hand, the electrons in the non-equilibrium plasma are at a higher temperature than other particles and thus the system is usually close to room temperature. In some common discharge methods for non-equilibrium plasma, like dielectric barrier discharge (DBD) and nanosecond repetitive pulse discharge (NRPD), electrical energy is firstly deposited into the electron movement, and then, through the collision of the energetic electrons with the gas molecules, excitation, ionization, and dissociation occur. However, due to the obviously lower gas temperature in DBD or NRPD, the cracking efficiency and yield are also limited. Therefore, these two methods are usually used together with heating or catalysts [1].

The present study used microwave plasma to crack ammonia for hydrogen production. A microwave plasma jet (MWPJ) is known to have a relatively high gas temperature (2000–5000 K) with relatively lower electron energy (<1 eV). Compared with DBD and NRPD, microwave plasma generally has a higher gas temperature, and thus catalysts are not required in this process. Moreover, since the reactant and the microwave resonate cavity are separated by the quartz tube, there is no reactant-electrode contact and thus no erosion.

2. Experimental setup

Figure 1 shows the experimental setup utilized in this work. A 2.45 GHz solid microwave source (GMS200W) and a surfatron device (Sairem, Surfatron60) were employed for MWPJ [2, 3]. To initiate the plasma jet, Argon gas (99.999% purity) was fed into the surfatron, and then the spark discharge breakdowns the argon gas

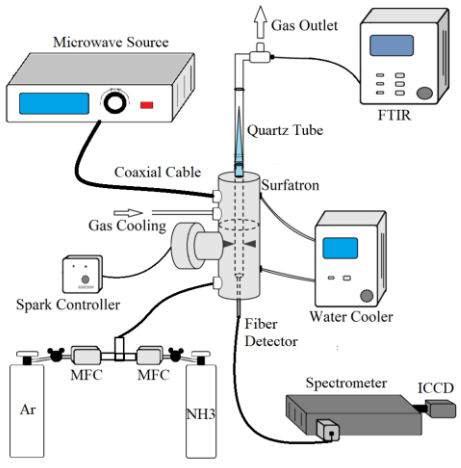

Fig. 1. Experimental setup.

providing some "seeding" electrons. These electrons absorb the microwave energy and collide with Ar causing a series of ionization, finally forming the plasma jet. The surfatron is cooled and sustained at room temperature using a water cooler. The quartz tube reactor is cooled using nitrogen flow. The ammonia (NH_3, 99.999% purity) is added after that the plasma jet is stabilized. The incident MW power is adjustable from 50 to 150 W, while the reflected power is limited to less than 10% of the incident power.

The physical characteristics of the plasma jet are investigated using optical emission spectroscopy (OES). Fourier Transform Infrared Reflectance Spectroscopy (FTIR) is used to analyze the gas product and calculate the NH_3 conversion.

3. Results and discussions

3.1 NH3 addition limitation

Figure 2 provides the limit of ammonia addition ($Limit_{NH3}$) with the total flow rate and microwave incident power. When NH_3 was further added beyond this limit, MWPJ could not be sustained anymore. It can be observed that $Limit_{NH3}$ increases with the incident microwave power, while it slightly decreases as the total flow rate increases.

3.2 Ammonia conversion ratio

Figure 3 shows the changes in the NH_3 conversion ratio with various total flow rates and incident microwave power. As the total flow rate increases from 1 SLPM to 5 SLPM, the conversion ratio at 50 W case obviously decreases from around 50 % to 10 %. The reason is that increasing the total flow rate decreases the mean gas temperature, and it also reduces the residence time of ammonia in the plasma region. With a total flow rate of 1L/min, increasing the microwave power to 100 W or higher, the ammonia is almost completely converted.

Figure 4 exhibits the relation between the NH_3 conversion ratio and energy density (defined as the incident microwave power divided by the total flow rate). Obviously, the ammonia conversion ratio and energy density almost show a directly proportional relationship. Once the input energy density is beyond 5.7 kJ/L, all the ammonia will be fully converted.

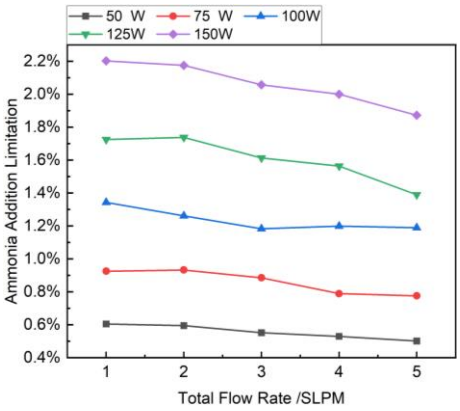

Fig. 2. Limit of ammonia addition under various total flow rates and microwave incident powers.

Figure 5 shows the ammonia conversion ratio against the ammonia content. It can be observed that the ammonia conversion ratio is almost independent of the ammonia content.

Figure 6 shows the hydrogen production rate calculated according to the data in Fig.5 under the assumption that the product of NH_3 conversion only includes hydrogen and nitrogen. It can be seen that the hydrogen production rates under different flow rates are very close. Therefore, considering the cost of the production, the higher ammonia content and lower total flow rate would be the better option for hydrogen production.

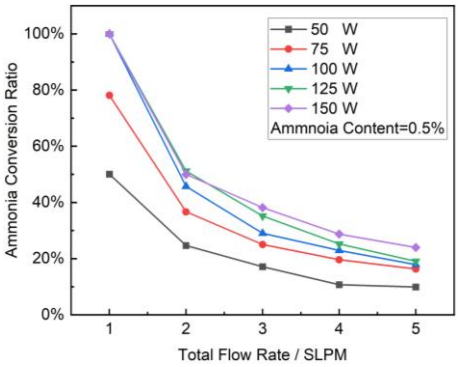

Fig. 3. Ammonia conversion ratio against total flow rate and microwave incident power.

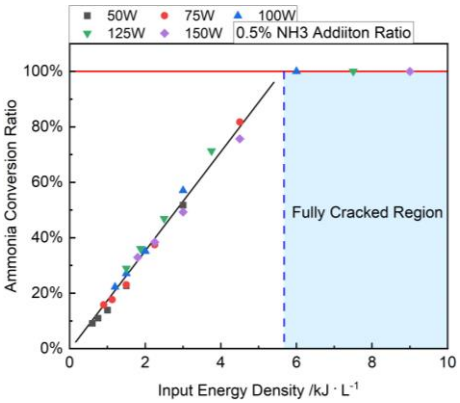

Fig. 4. Ammonia conversion ratio against input energy density.

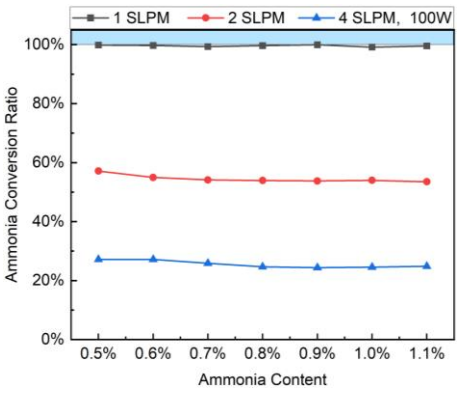

Fig. 5. Variation of ammonia conversion ratio as a function of ammonia content in the mixture.

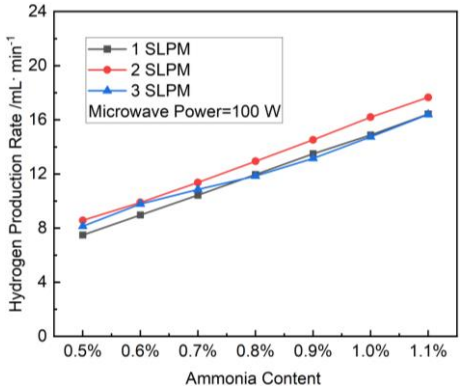

Fig. 6. Variation of hydrogen production rate as a function of ammonia content in the mixture.

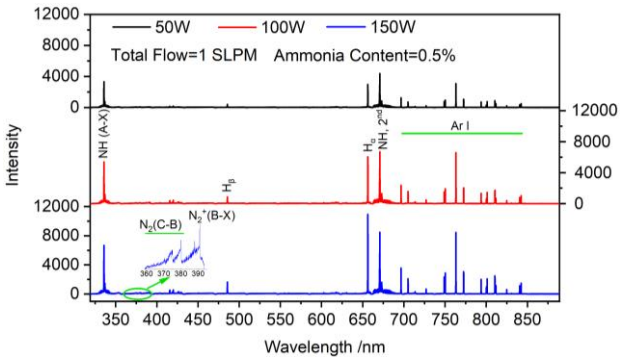

Fig. 7. Emission spectra with 50 W, 100 W, and 150W microwave input power at 1L/min of the total flow rate.

3.3 Spectrum

Figure 7 provides the typical emission spectra under 1L/min when 3 different incident powers were used. Based on the spectra, we identified the spectral lines of Ar (in the range of 690-850 nm), NH (A-X: at ~336 nm), and NH 2nd in the second order of the grating near 672 nm, H_α (at 656.3 nm) and H_β (at 486.1 nm), N_2(C-B: 360-380 nm) and N_2^+(B-X: 391.9 nm). The observed emission spectra indicated that the initial ammonia was successfully decomposed by the Ar plasma to hydrogen with intermediate NH and nitrogen radicals. As the power increases from 50 W to 150 W, the spectrum intensities of the mentioned transitions obviously increased. Note that since ammonia is colorless and the spectrum was collected from the bottom of the surfatron, there is no significant interference in the visible range.

Figure 8 shows the intensity of critical transitions under various total flow rates. As the total flow rate was increased from 1 SLPM to 5 SLPM, NH intensity increased accordingly, while the H lines decreased slightly. It is worth noting that the Ar lines almost did not show obvious differences despite of the fluctuations.

Figure 9 shows the plasma rotational temperature calculated by fitting the N_2^+(B-X) spectral line under different total flows using Specair software. The rotational temperatures slightly decreased with the increase in the total flow, but for all conditions, the rotational temperature was over 5000 K, indicating that the temperature in the present case is not

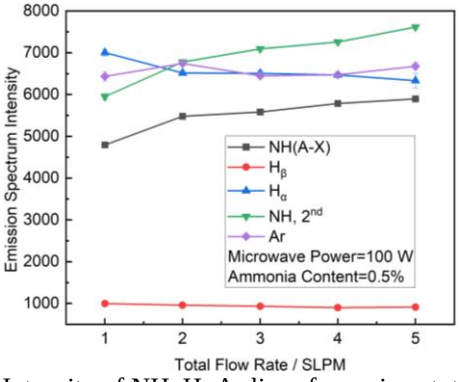

Fig. 8. Intensity of NH, H, Ar lines for various total flow rates (1–5 SLPM).

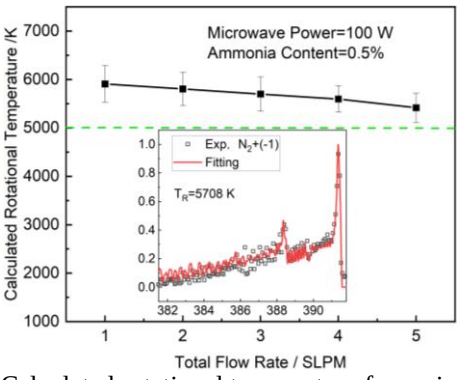

Fig. 9. Calculated rotational temperature for various total flow rates (1–5 SLPM).

the critical factor that influences the ammonia conversion ratio. In other words, the ammonia residence time in the plasma region especially in the region near the microwave resonate cavity, is a more dominant factor for ammonia conversion.

4. Conclusion

We experimentally studied the performance of a microwave-powered surfatron discharge plasma for ammonia conversion based on the measurement through FTIR and OES under various conditions. We found that the ammonia can be completely converted at 100 W microwave power with 1 SLPM total flow rate. This high conversion ratio was almost independent of the ammonia content in the mixture when it was within the ammonia addition limitation. In addition, the ammonia conversion ratio and energy density show a directly proportional relationship. The ammonia residence time in the plasma region, especially in the region near the microwave resonate cavity, was found to be a dominant factor for the ammonia conversion.

5. Reference

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